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Corroles as receptors in liquid membrane electrodes and their potentiometric response towards salicylic acid

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Abstract

Here, we report on the application of corroles as analytically active compounds in liquid membrane electrodes (ISE) that are sensitive towards salicylic acid and salicylate.

The potentiometric signals generated by corrole-incorporated ISEs strongly depend on the pH of the aqueous sample solution and the membrane composition, such as the presence of lipophilic sites. Corrole incorporating ISEs are characterised by a low detection limit (4.0×10^{-5} M) and a wide linear range (4.0×10^{-5} to 5.3×10^{-3} M). Also, they are free from interference versus other organic anions.

The mechanism of the generation of the potentiometric signals of corrole incorporating ISEs in the presence of salicylate anion, as well salicylic acid, will be discussed.

Keywords: Corroles; Salicylic acid; Liquid membrane; Potentiometric response

1. Introduction

Anion recognition and sensing, since around 1970, are still the subject of intensive research in many laboratories. Recently, the synthesis of new receptors that are able to selectively recognise anions has been reported [1–3]. Nevertheless, problems concerning anion-selective electrodes still remain to be solved in view of a very fast growing demand in food quality control, medical and environmental monitoring laboratories [4,5].

The main reason of the difficulties associated with developing of anion-sensitive ISEs is the aqueous media in which electrodes are expected to be applied.

Therefore, a strong interaction between ionophore and anions is required in order to form successfully the supramolecular host–guest complex at the aqueous/organic interface. The energy of the complex formation should be high enough to allow for the anion dehydration and transfer from water sample solution to the surface of polymeric membranes [6,7]. The energy of the complex creation between the host and guest molecules is strongly correlated with the number of types of interaction between them. According to the type of interaction, the receptors can be divided in two groups [2].

In the first one are receptors which employ hydrogen bonds and electrostatic interactions. To this group belong receptors containing amide, pyrrole, urea, polyammonium macrocycles, guanidinium, amidinium and thiouronium [2].

To the second group belong Lewis acid receptors containing a metal cation in their structures. The cation in these receptors plays a number of different roles: coordination site for the anion, non-coordinating reporter group that signals the presence of the anion by perturbation of its physical properties (i.e. by changes in redox or spectroscopic properties) and an element to withdraw electron density from the π electron system [3].

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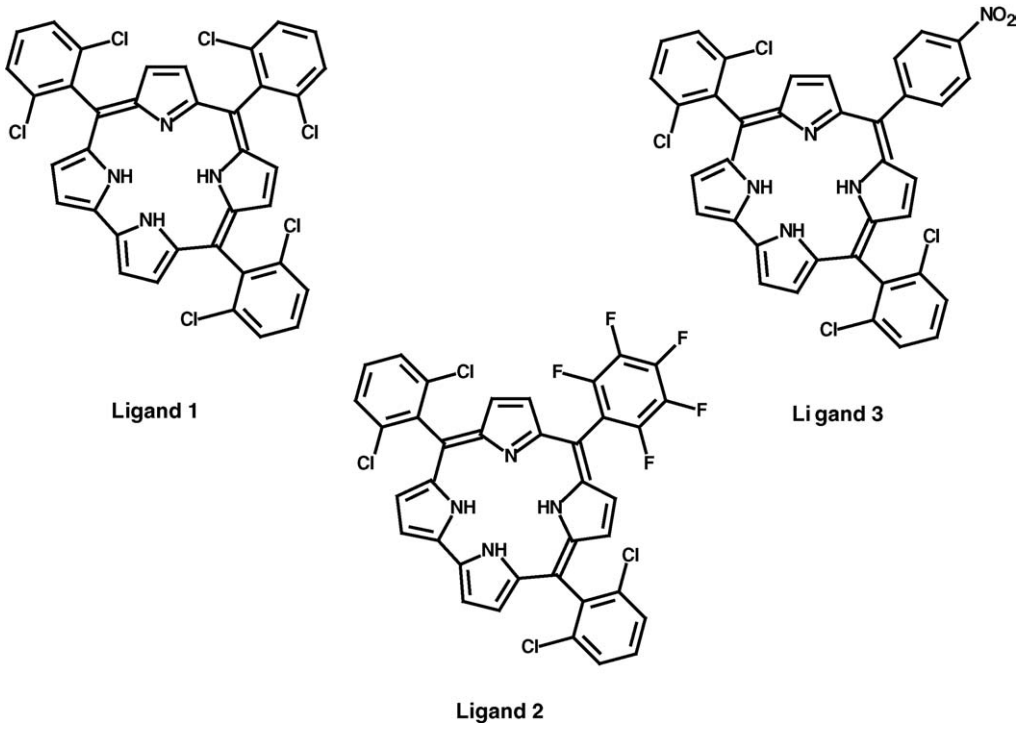


Fig. 1. Chemical structures of corroles **1–3** under study.

The main objective of the present work was to explore corrole derivatives as ionophores for salicylate-selective ISEs.

Corroles are cyclic tetrapyrroles with an aromatic 18π electron system, which contains one direct linkage between two adjacent pyrrole rings just as the corrine skeleton in Vitamin B_{12}. Corrole is formally derived from the porphyrin macrocycle by deleting one of the four meso carbons. Corroles display unusually high N–H acidity relative to porphyrins and other related macrocycles [8–10]. This feature makes them very interesting and useful for utilisation as ionophores in ISEs. As a receptor, corrole could be classified to the first group. The structures of corroles studied are introduced in Fig. 1.

2. Experimental

2.1. Reagents and materials

Corroles were synthesised following previously reported methods [8]. The 2-fluorophenyl-2-nitrophenyl ether (FNDP) used as membrane solvent and poly(vinyl chloride) (PVC; n_{av} = 1100) used as the polymer matrix, were purchased from Wako (Japan). Salicylic acid, 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid (HEPES), citric acid, lithium acetate and potassium chloride were purchased from Sigma–Aldrich (Poznań, Poland). Tridodecylmethylammonium chloride (TDDMACl) was purchased from Fluka, potassium tetrakis(*p*-chlorophenyl)borate (K-TpCPB) was purchased from Dojindo (Japan). Tetrahydrofuran (THF) was purchased from POCh-Gliwice, Poland, and was distilled over solid NaOH just before use.

All the samples and buffer solutions were prepared with deionised water with a resistivity of 18.2 MΩ cm.

2.2. Electrode preparation and potentiometric measurements

The composition of the PVC matrix membranes based on corroles was as follows: 1 wt.% ligand under study (2.0 mg), 66% FNDP (132 mg) and 33% PVC (66 mg). Membranes with ionic salts contained 50 mol% salt (T-DDMACl or K-TpCPB) versus ligand. The mixture thus prepared was dissolved in approximately 2 ml freshly distilled THF. The resulting solution was placed into a glass ring of 30 mm diameter for 24 h to allow THF evaporate to obtain membranes with standard thickness of ca. 100 μm. Circles of 6 mm diameter were cut from the resulting membrane and mounted on a liquid membrane type Philips ISE body (Glasblästerei Möller, Zűrich, Switzerland).

The electrode cell for the potential measurements was as follows: Ag/AgCl|0.1 M KCl|membrane|sample solution||1 M CH_3COOLi||3 M KCl|Ag/AgCl.

Potentiometric measurements were performed at room temperature (ca. 20 °C) by means of a multi channel station pH-meter made by Donau-Lab (Warsaw, Poland). The reference electrode was a double junction Ag/AgCl electrode.

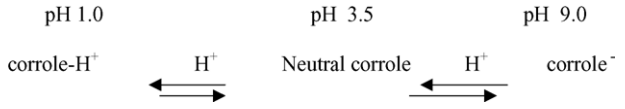
2.3. Control of penetration of salicylic acid through the corrole membrane

For experiment on the penetration of salicylic acid through corrole membrane, a utensil Teflon with two cells was used. The cells were separated by a piece of membrane containing corrole **1**. The 1.0×10^{-3} M salicylic acid solution in a buffer pH 2.0 or 4.5 was placed in the first cell. In the second cell was placed 0.1 M KCl, used as an inner solution in the ISEs.

The transport of salicylic acid through the corrole membrane was monitored by a UV–vis 1240 spectrophotometer (Shimadzu, Kyoto, Japan) at regular time intervals.

3. Results and discussion

The corroles, because of their unusually high N–H acidity relative to porphyrins, could exist, depending on the pH, in a neutral, deprotonated and protonated form [9,10]:



(1)

Because of this, the effect of protons on the response of the membranes incorporating corroles was examined. The potentiometric response was measured as the pH was changed by dropwise addition of 100.0 mM NaOH to 10.0 mM H_3PO_4. The solution of NaOH contained 10.0 mM Na_3PO_4 in order to maintain the total concentration of PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$ constant. Fig. 2 illustrates the representative results obtained for the membrane modified with corrole **1**-ISE (curve A). Other ligands **2** and **3** displayed similar behaviour.

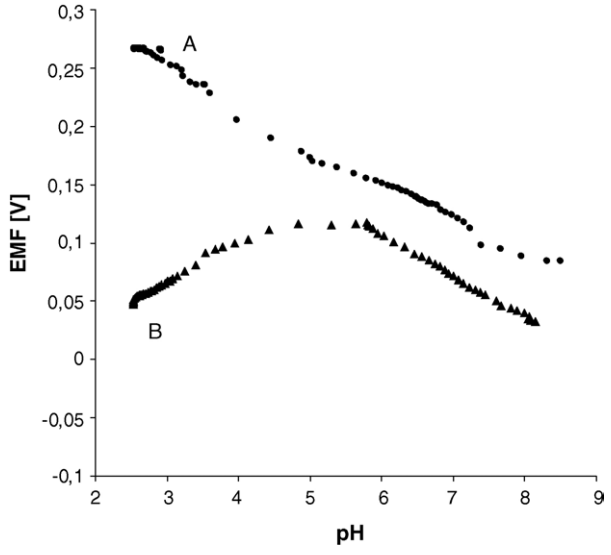


Fig. 2. Potential vs. pH curves obtained by an electrode based on corrole **1** (A) in the absence of anionic guest and (B) in the presence of salicylic acid.

The curve A showed that the membrane responded towards the pH of the sample solution with a slope of ca. 39 mV/log C in the pH range from 5.0 to 2.5. Within the pH range from 7.0 to 5.0, the slope was smaller, ca. 22 mV/log C. In the alkaline solution, the membrane showed almost no response towards pH change. This phenomenon could be interpreted by the gradual protonation of corrole in the membrane with the decrease of pH solution.

The experiment was repeated in the presence of a fixed concentration (1.0×10^{-2} M) of sodium salicylate (Fig. 2, curve B).

Within the pH range from 8.8 to 5.8, the membrane potential increased with a slope of ca. 35 mV/log C. With the decreasing of pH below 5.8, the membrane potential decreased in the presence of salicylic acid. This suggests that in the acidic solution (pH 5.8–2.5), an interaction between corroles incorporated into the membrane and salicylic acid present in the aqueous phase occurred. At pH 3.0, the potential difference of corrole **1** membrane caused by the presence of salicylic acid was ca. 174 mV. The results obtained indicate that salicylic acid starts to interact with corroles at pH 5.5.

The response properties of ISEs based on ion carriers are strongly influenced by the membrane composition, in particular, by presence of ionic sites [11–14]. In the case of ISEs based on neutral carriers, ionic sites with the charged sign opposite to that of primary ions are necessary to obtain a Nerstian response, to decrease the membrane resistance, to reduce the co-ion interference and to improve the detection limit and selectivity. On the other hand, in ISEs based on electrically charged carriers, ionic sites with the same charge sign as the primary ions are recommended.

The corroles could exist in both forms, so two type of ionic sites were examined: anionic K-TpCPB and cationic TDDMACl.

The corrole membranes with anionic lipophilic sites showed no response towards salicylate in all of the investigated pH range (results not shown).

On the other hand, the addition of cationic lipophilic salts improved the detection limit and sensitivity.

Fig. 3 illustrates the potentiometric response of corrole **1** membrane incorporating additionally 50% versus ionophore TDDMACl towards the change of pH of the sample solution: without salicylic acid (curve A) and in the presence of 1.0×10^{-2} M salicylic acid (curve B).

The curve A showed that the membrane responded towards pH of the sample solution with a slope of ca. 43 mV/log C in the pH range from 7.0 to 2.5 slightly higher than corrole **1** membrane without cationic sites (Fig. 2).

In the alkaline solution, the membrane additionally incorporating TDDMACl showed almost no response towards pH change, similar like was observed for the membrane containing only corrole **1** (Fig. 2).

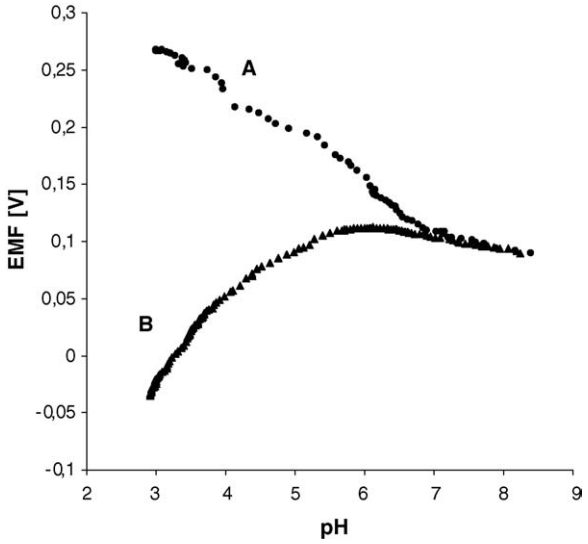


Fig. 3. Potential vs. pH curves obtained by an electrode based on corrole **1** and TDDMACl (A) in the absence of anionic guest and (B) in the presence of salicylic acid.

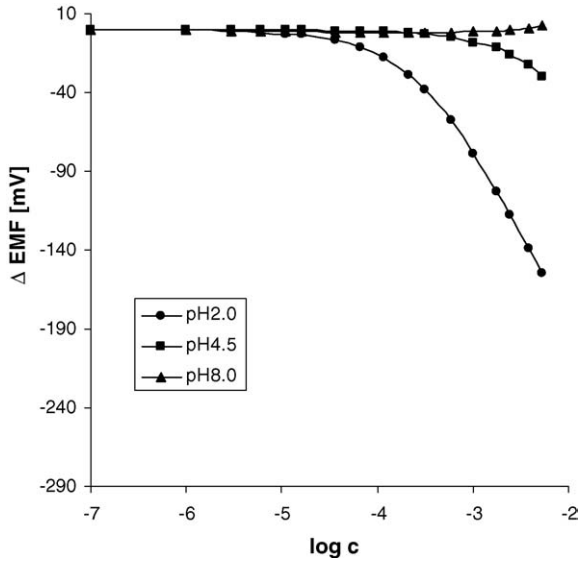


Fig. 4. Potential vs. concentration curves obtained by electrodes doped with corrole **1** towards salicylic acid and salicylate measured at pH 2.0, 4.5 and 8.0.

In the presence of salicylic acid, the decreasing of the membrane potential with the decreasing of pH occurred in the pH range from 6.8 to 2.5 (Fig. 2, curve B). The interaction of salicylic acid with membrane incorporating only corrole **1** occurred in more acidic solution at pH 5.8 (Fig. 2, curve B). Also, the presence of cationic salts in the corrole **1** membrane caused a larger potential decrease (ca. 290 mV) caused by the interaction with salicylic acid, in comparison with a corrole **1** membrane without any additives. The membrane incorporating only TDDMACl also responds towards anionic guests, as an ion-exchanger. This might be the reasons that corrole-ISEs additionally incorporated with TDDMACl displayed better sensitivity towards salicylate.

The lack of response of corrole-ISEs incorporated additionally with anionic lipophilic sites may be was caused by some specific interaction between corrole host and tetrakis(*p*-chlorophenyl)borate anion. We will explore this phenomenon future in our laboratory.

The possibility of transport of salicylic acid or salicylate across the corrole membrane was checked by performing long-term experiments in which two solutions: (1) composed with 1.0 mM salicylic acid in the presence of 10.0 mM buffer (pH 2.0 or 4.5) and (2) 0.1 M KCl were separated by membrane incorporating corrole **1**. The presence of salicylic acid in KCl solution was monitored by UV–vis measurements. The 0.1 M KCl solution, used as inner solution in ISEs, was free of salicylic acid during 100 min. The one run of potentiometric measurements last ca. 30 min. So, it might be stated that during this time, the composition of inner solution was constant.

The addition of buffer to the inner solution showed no influence on the potentiometric response towards salicylic acid or salicylate.

Therefore, only 0.1 M KCl was used as the inner solution for all potentiometric measurements presented.

Based on the results obtained in the experiment exploring the membrane potential versus pH change of the sample solution, the calibration curves for salicylic acid measured with corrole membranes were done in buffered solution at different pH values (pH 2.0, 4.5 and 8.0).

In general, the presence of TDDMACl improved the potentiometric response of corrole **1** membrane towards salicylic acid and the response increased with decreasing pH. The strongest response towards salicylic acid was observed for both type of membranes at pH 2.0 (Figs. 4 and 5). Similar results have been received for all of the investigated ligands (results not shown). At these pH conditions, salicylic acid exists in water solution as the neutral compound (Table 1) and the corrole in the membrane might be partly protonated [9].

The detection limit for the corrole **1** membrane at pH 2.0 was 2.0×10^{-4} M.

The presence of TDDMACl lowered the detection limit (4.0×10^{-5} M). Both types of membranes responded towards the neutral form of salicylic acid with a very high slope (93 and 133 mV/log C for corrole **1** and corrole **1** + TDDMACl, respectively). The other ISEs incorporating corroles **2** and **3** displayed similar properties (results not shown). Thus, the functional groups attached to the corrrole ring have no crucial influence on the phenomenon studied.

The origin of very high response of corrole-ISEs towards neutral form of salicylic acid probably comes from the different mechanism of the potentiometric signal generation. In this particular case, target analyte exists in the neutral form. The "anionic" potentiometric response probably was generated by proton ejection from the corrole–salicylic acid supramolecular complex formed at the interface to the aqueous phase.

Table 1
Influence of pH of aqueous sample solution on the detection limit and slope of corrole **1**-incorporated ISE-sensitive towards salicylic acid and salicylate

pH	Salicylic acid		Detection limit [M]		Slope [mV/log C]	
	Neutral form [%]	Dissociated form [%]	Corrole **1**	Corrole **1** + TDDMACl	Corrole **1**	Corrole **1**+ TDDMACl
2.0	90.3	9.7	2.0×10^{-4}	4.0×10^{-5}	93.3	132.5
4.5	2.9	97.1	1.0×10^{-3}	1.0×10^{-4}	38.8	79.1
8.0	0.0	100.0	No response	–	No response	–

Detection limit [M]

pH	Corrole **1**	Corrole **2**	Corrole **3**	Corrole **1** + TDDMACl	Corrole **2** + TDDMACl	Corrole **3** + TDDMACl
pH 2.0	2.0×10^{-4}	4.8×10^{-4}	1.9×10^{-4}	4.0×10^{-5}	5.3×10^{-5}	2.8×10^{-5}
Slope [mV/log C]						
pH 2.0	93.3	90.4	107.1	132.5	134.1	125.0

The stoichiometry of this reaction probably determined the response slope.

At pH 4.5, the salicylic acid exist in the solution almost totally in the dissociated form. In these conditions, the detection limits were: 1.0×10^{-3} M for corrole **1** membrane and 1.0×10^{-4} M for membrane incorporated additionally with TDDMACl (Figs. 4 and 5). At this pH, the slopes were lower than in acidic condition: 38.8 and 79.1 mV/log C for both type of membranes, respectively (Table 1).

No potentiometric response towards salicylate was observed in alkaline solution at pH 8.0 (Fig. 4). In these conditions, the target analyte exists in the anionic form, but the host molecule, corrole, incorporated into the organic phase, probably exists mostly in its deprotonated, anionic form [9]. This might be the reason of the lack of potentiometric response in alkaline solution.

The important parameter concerning the ISEs is the response time. Fig. 6 illustrates the potential changes of corrole **1** incorporating ISE upon the salicylic acid concentration changes. This new type of salicylate-sensitive ISE is characterised by a reasonable response time, ca. 100 and 60 s, in the lower and higher concentration range, respectively (Fig. 6). These response times suggest that formation of supramolecular complex between corrole host and salicylic acid guest, responsible for potentiometric signal generation, occurred at the membrane phase, adjacent to the aqueous.

In Table 2, the values of the potentiometric selectivity coefficients of membrane sensors based on corrole **1**, and corrole with TDDMACl determined by the matched potential method are collected [15,16].

The presented membranes are able to recognise salicylic acid with good selectivity. The selectivity sequence is different than so-called Hofmeister pattern. The common inorganic and organic anions caused low interference on the target analyte. The addition of TDDMACl in some cases improved the selectivity of the corrole membranes.

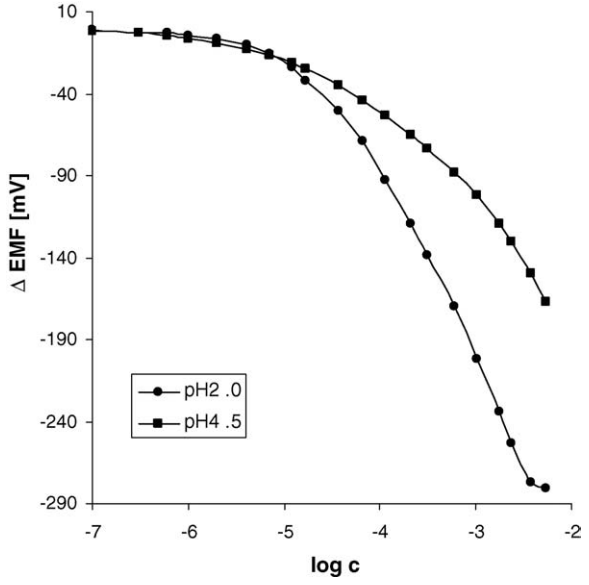


Fig. 5. Potential vs. concentration curves obtained by electrodes doped with corrole **1** and TDDMACl towards salicylic acid and salicylate measured at pH 2.0 and 4.5.

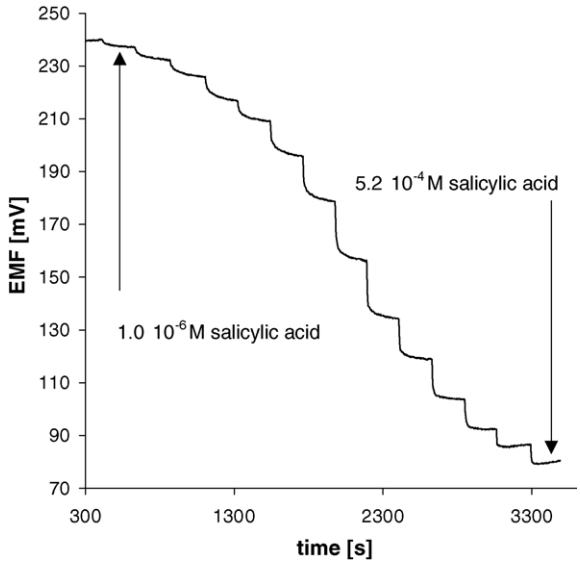


Fig. 6. The potential changes of corrole **1** incorporating ISE upon concentration changes of salicylic acid vs. time.

Table 2
Potentiometric selectivity coefficients of ISEs based on corrole **1**

Interferents	$\log K^{MPM}_{i,j}$			
	Corrole **1**		Corrole **1** and TDDMACl	
	1.0×10^{-4} M[a]	1.0×10^{-3} M[b]	1.0×10^{-4} M[a]	1.0×10^{-3} M[b]
Citric acid	$\ll 0$	$\ll 0$	$\ll 0$	$\ll 0$
Oxalic acid	$\ll 0$	$\ll 0$	-2.87 ± 0.17	$\ll 0$
Fumaric acid	$\ll 0$	$\ll 0$	$\ll 0$	$\ll 0$
Gallic acid	-0.78 ± 0.14	$\ll 0$	$\ll 0$	$\ll 0$
Sorbic acid	-1.59 ± 0.19	-1.25 ± 0.14	-2.00 ± 0.16	$\ll 0$
Benzoic acid	-1.16 ± 0.14	-1.12 ± 0.16	-1.20 ± 0.14	-0.98 ± 0.13
Maleic acid	-0.95 ± 0.09	-1.11 ± 0.08	-0.46 ± 0.23	-0.76 ± 0.13
Acetylsalicylic acid (aspirin)	-0.94 ± 0.09	-1.10 ± 0.09	-0.23 ± 0.10	-0.34 ± 0.12
Cl^-	$\ll 0$	$\ll 0$	-3.06 ± 0.18	$\ll 0$
F^-	-0.88 ± 0.09	×	-0.66 ± 0.07	×
NO_3^-	-1.27 ± 0.15	-2.38 ± 0.20	-0.29 ± 0.08	-0.79 ± 0.09
PO_4^{3-}	$\ll 0$	$\ll 0$	$\ll 0$	$\ll 0$

$\log K^{MPM}_{salicylic\ acid,\ j}$ were determined by matched potential method (MPM) [15,16] in mixed solution 1.0×10^{-2} M H_2SO_4–Na_2SO_4 (pH 2.0). $\log K^{MPM}_{salicylic\ acid,\ j}$ were calculated for ΔEMF = 2.0 mV. Mean value of three repetition are given; ×: the potential was constant till 6.3×10^{-3} M of interfering salt, next cationic potentiometric response was observed. a,b–Concentration of salicylic acid in the background solution.

Based on the parameters, such as limit detection, slope, response time and selectivity coefficients, corroles-incorporated ISEs might be recommended for practical application, for example for the determination of salicylate in human serum [17].

The content level of salicylate in human serum is in the range 3.0×10^{-4} M, so the corroles-incorporated membranes are suitable for its analysis.

The sensors presented could be added to the group of salicylate-sensitive electrodes based on: chromium(II) porphyrin [17], guanidinum [18], Sn(IV)- and Mo(V)-porphyrins [19–21], bismetalloporphyrins [22] or Sn(IV)salophens [23]. All of them responded only towards salicylate anions, with the detection limits ca. 10^{-4} M.

To our knowledge, the corrole-ISE is the first potentiometric sensor-sensitive towards both salicylate and salicylic acid with good detection limit of ca. 10^{-5} M.

The corrole-ISEs responded towards analytes studied reversibly.

The calibration curves for salicylic acid or salicylate were made several times, and after conditioning, a starting potential in the buffer solution was received.

As was already stated, the response of membranes studied strongly depends on the pH conditions. The probable reasons for this are the changes of chemical forms of the target molecules as well as changes of chemical form of ligand which occur upon pH changes. Also, the mechanism of the potentiometric signals generation is probably different for sample solutions at pH 2.0 and >3.5.

At pH higher than 3.5, the corrole exists in the neutral form in the membrane phase. At this pH condition, salicylic acid is dissociated. Therefore, the formation of a supramolecular complex via hydrogen bonds between the salicylate anions and corrole molecules located on the surface of the membrane phase leads to a charge separation on the membrane/water interface, because the salicylate ions are transferred from the water to the membrane surface.

In the solution at pH 2.0, salicylic acid exists only in the neutral form. The mechanism of signal generation, in this condition, probably relies on two steps. In the first step, the supramolecular complex between corrole–H^+ or/and corrole and the neutral form of salicylic acid is formed via hydrogen bonds which involve hydrogen atoms from host molecule and the free electron pair from the –COOH group of the guest. As a consequence, the acidity of the –COOH group increases. In the second step, the proton from this supramolecular complex might be dissociated and shifts from the surface of the organic phase to the water phase. This last step is responsible for the anionic potentiometric response of the corrole membranes towards neutral molecules of salicylic acid. The similar mechanism we have observed for membranes modified with calix [4] pyrroles [24–26], macrocyclic polyamines [27], calixarenes [28] and corroles [29,30] after their stimulation with neutral form of phenol derivatives.

4. Conclusions

ISEs incorporated with corroles are able to selectively recognise both salicylic acid as well salicylate.

The potentiometric signals generated by corrole-ISEs in the presence of salicylic acid depend on the pH of the sample solutions and on the membrane composition.

The corrole-ISEs demonstrated a low detection limit ($\sim 4.0 \times 10^{-5}$ M), wide linear range (4.0×10^{-5} to 5.3×10^{-3} M) and low interference versus other common anions. Therefore, they might be applied for salicylate determination in real samples (research in progress).

Acknowledgements

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